BIOMIMETIC CATALYSTS: APPLICATION OF COORDINATING COMPLEXES CONTAINING AN ASYMMETRIC COORDINATING LIGAND

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INTRODUCTION

The catalytic conversion of methane from natural gas into a readily transportable liquid fuel is a research area that is currently attracting considerable attention. This is a difficult transformation from a thermodynamic viewpoint since methane is a relatively unreactive substance and chemicals derived from methane are substantially more reactive than methane itself. Thus, no industrial process to date has been able to convert methane to liquid products in high yield.

One of the more studied process is the oxidative coupling of methane to higher hydrocarbons and olefins. To date no laboratory processes have come close to a yield necessary for an economically viable process. Modeling studies suggest that a theoretical ceiling in overall yield exists as the rate constant of a catalyst is increased[1]. The rate constant of the catalyst must be sufficient to overwhelm the non-specific gas phase reactions but low enough to prevent over oxidation. In theory this limits the yield to about 35%.

Because of this perceived limitation in heterogeneous catalysts, we undertook a program to take advantage of the selectivity already known to exist in a bacterial enzyme system. A group of aerobic soil/water bacteria called methanotrophs can efficiently and selectively utilize methane as the sole source of energy and carbon for cellular growth.[2] The first reaction in this metabolic pathway is the conversion of methane to methanol and is catalyzed by the enzyme methane monooxygenase[3] (MMO). (Figure 1) Of the many liquid products available directly from methane, methanol is one of the more technologically important. It can be easily converted to liquid hydrocarbon transportation fuels, used directly as a liquid fuel itself, or serve as a feed stock for fine chemicals production.

Microorganisms can produce MMO in two distinct forms: a membrane-bound particulate form or a discrete soluble form. The soluble form contains an oxygenase subunit, whose active site includes a binuclear iron center.[4,5,6] The

complete details of the structure of the active site are not known. However, the general description of the iron site in the soluble form is a binuclear cluster containing some type of μ-oxo ligand between the iron atoms. The remaining ligands (derived from adjacent amino acid residues) coordinate to the metals through nitrogen or oxygen and the Fe-Fe distance is 3.4 Å. The best description of the amino acids coordinating the binuclear iron center is surmised by the close amino acid sequence homology between MMO and ribonucleotide reductase[7], an enzyme containing a binuclear iron center whose X-ray crystal structure has been determined[8].

Compared to the soluble form of MMO the particulate form is poorly characterized and is thought to contain copper at the active site. This form is also active in methane oxidation in the biological system, and may be selectively produced by manipulating the bacterial growth conditions.[9]

Our work centers on the characterization of the structure/activity relationships of the particulate form of MMO and synthesis and characterization of inorganic/organic chemical models of MMO (both particulate and soluble). We have focused on the synthesis of an asymmetrical, binuclear chelating ligand possessing an alkoxo group that can serve as a bridging μ-oxo ligand. The advantage of such a ligand system is twofold: (a) metal complexes of an asymmetric binuclear ligand will provide coordinate unsaturation at only one metal resulting in focused substrate reactivity at that site and (b) a single ligand with binuclear coordination provides a more robust environment for metal oxidation state changes and accompanying chemical reactions. These complexes are being evaluated for their ability to oxidize methane and other hydrocarbons.

EXPERIMENTAL

The synthesis of the chelating ligand HMeL obtained by a five step procedure in ~35% overall yield is outlined in Scheme 1. Mono and binuclear copper complexes of HMeL were prepared by dissolving 100 or 200 mole% of cupric perchlorate with 100 mole% HMeL and sodium acetate in methanol, as shown in Scheme 2. The crude materials were recrystallized by vapor diffusion of ethyl ether in acetonitrile and chemically characterized, including single crystal X-ray crystal structure[10].

Catalytic reactivity was determined under atmospheric pressure and ambient temperature. Cyclohexane as the hydrocarbon substrate, hydrogen peroxide the oxidant, and a metal complex were employed in ratios of 1000:100:1 respectively with final catalyst concentration 9.0×10^{-4}M. $Cu(BF_4)_2$, $Cu[HMeL][ClO_4]_2$, or $[Cu_2\text{-MeL-OAc}][ClO_4]_2$ (4.5×10^{-5} moles) were dissolved in acetonitrile and placed Fisher-Porter reaction bottle. A mixture of cyclohexane (4.5×10^{-2} moles) and 30% hydrogen peroxide (4.5×10^{-3} moles) in acetonitrile was added to the catalyst solution with vigorous stirring at T=0. Aliquots (1mL) were removed periodically and a portion was analyzed by GC/MS for

cyclohexanol/cyclohexanone content with the remainder being titrated with a standard solution of potassium permanganate to determine hydrogen peroxide conversion.

RESULTS

Scheme 1 shows the synthetic route for the prototype binuclear chelating ligand, HMeL. Elemental analysis and NMR studies confirm the composition and structure of the ligand. It possesses a hydroxyl functionality that could serve as a bridging alkoxo group and aliphatic and aromatic nitrogen coordination groups (benzimidazole). We expected that one metal ion would be coordinated by one aliphatic nitrogen and two imidazole nitrogens and bridged by the hydroxy group to another metal coordinated by one aliphatic nitrogen and one imidazole nitrogen. This structure establishes a basis for coordinate asymmetry. Additional ligands to fulfill the coordination requirements of the metals would be available from the solvent or by the addition of acetate.

HMeL will readily binds to one mole of Cu(II) to produce a mononuclear complex (Scheme 2). Addition of two moles of copper does not alter the resulting product, as formation of the mononuclear complex appears to be independent of copper concentration. Addition of 200 mole% of copper to HMeL in the presence of 200 mole% of acetate gives rise to a binuclear complex. One mole of the acetate is necessary to fulfill the coordination requirements of Cu(II) and he other to act as a Lewis base to assist in removing the hydroxyl proton on HMeL. The mononuclear complex may be readily converted to the binuclear complex by the addition of copper and acetate. This suggests the possibility that asymmetric binuclear complexes may be generated with different metals in specific positions.

One coordination site at one copper center of the binuclear Cu(II) complex is available to bind with extraneous ligands. This was shown by forming a stable complex between the binuclear Cu(II) complex and azide ion, whose structure was confirmed by solving the X-ray crystal structure. We expect that in a catalytic system that the vacant coordination site will be available to bind and activate oxygen, hydrogen peroxide, or other oxidizing agents.

These complexes were evaluated for their ability to oxidize cyclohexane and to disproportionate hydrogen peroxide and compared to unchelated Cu(II) under the same conditions. The results are presented in Table 1. Neither the unchelated Cu(II) or the mononuclear complex is capable of either disproportionating hydrogen peroxide or oxidizing cyclohexane. However, the binuclear Cu(II) complex is capable of oxidizing cyclohexane to a mixture of cyclohexanol and cyclohexanone, as well as disproportionating hydrogen peroxide. It is not clear if only the vacant binding (peroxide binding) site in sufficient for peroxide activation or if the coupled copper ions possess unique redox properties. These data show the proof-of-principal that these coordinately

asymmetric complexes will function as biomimetic catalysts and that they have the ability to oxidize hydrocarbons.

CONCLUSIONS

Our catalyst development effort has gone one full cycle in the design, synthesis and evaluation of a binuclear, coordinately-asymmetric coordination complex. Unchelated and a mononuclear copper complex do not show catalytic properties to activate hydrogen peroxide or to oxidize cyclohexane. However, the binuclear copper complex tested was capable of activation hydrogen peroxide and the presumed oxo-copper intermediate was able to oxidize cyclohexane. We are using this ligand as a starting point to synthesize new catalysts/ligands. Specifically, complexes with other metals (iron) and complexes with additional ligand groups and with varying oxygen to nitrogen contact atoms will be prepared.

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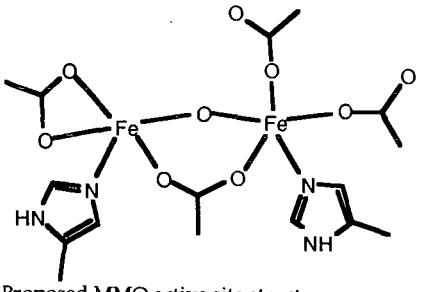
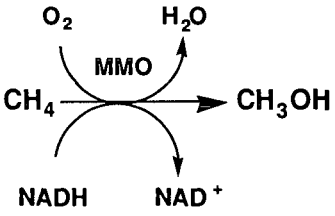
Table 1. Oxidation of Cyclohexane

Complex	% H_2O_2 Converted	Products	Turnover
$Cu(BF_4)_2 \cdot 6\ H_2O$	0 (24 hrs)	--	--
$[CuMEL][ClO_4]_2$	0 (48 hrs)	--	--
$[Cu_2MELOAc][ClO_4]_2$	40 (48 hrs)	cyclohexanol cyclohexanone	3

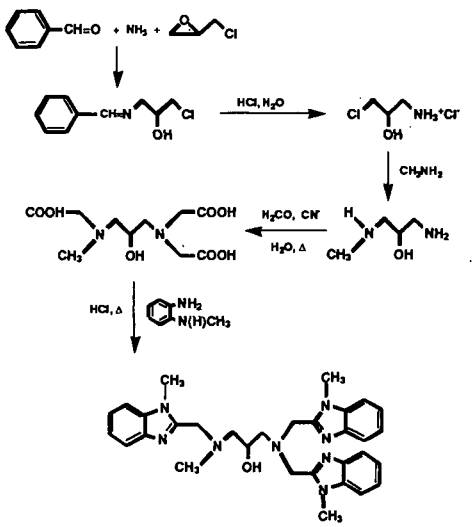


Proposed MMO active site structure

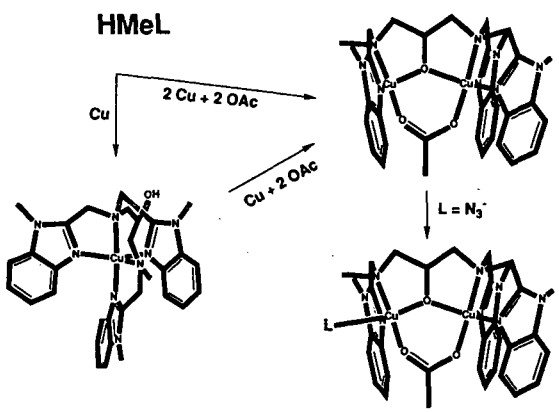


MMO Function

Figure 1. Structure/Function of MMO enzyme



Scheme 1. Synthesis of HMeL



Scheme 2. Copper Chelation by HMeL